A HIGH-STRENGTH AUSTENITIC STAINLESS STEEL STRIP EXCELLENT IN FLATNESS OF SHAPE AND ITS MANUFACTURING METHOD

BACKGROUND OF THE INVENTION

The present invention relates to a high-strength meta-stable austenitic stainless steel strip composed of a dual-phase structure of austenite and martensite excellent in flatness of shape with Vickers hardness of 400 or more, and also relates to a manufacturing method thereof.

Martensitic, work-hardened or precipitation-hardened stainless steel has been used so far as high-strength material with Vickers hardness of 400 or more.

Martensitic stainless steel such as SUS 410 or SUS420J2 is material hardened by quenching from a high-temperature austenitic phase to induce martensite transformation. Since the steel material is adjusted to Vickers hardness of 400 or more by heat-treatment such as quenching-tempering, its manufacturing process necessitates such the heat-treatment. The steel strip unfavorably reduces its toughness after quenching and changes its shape due to the martensite transformation. These disadvantages put considerable restrictions on manufacturing conditions.

Work-hardened austenitic stainless steel such as SUS 301 or SUS 304 is often used instead, in the case where deviation of shape causes troubles on usage. The work-hardened austenitic stainless steel has an austenitic phase in a solution-treated state and generates a deformation-induced martensite phase effective for improvement of strength during cold-rolling thereafter.

Although a shape of a steel strip is flattened by cold-rolling, dependency of hardness on a rolling temperature is too big, and the shape is irregularly varied along a lengthwise direction of the steel strip. In this consequence, it is difficult to flatten the shape of the steel strip under stable conditions by cold-rolling from an

industrial point of view.

A degree of transformation from austenite to deformation-induced martensite depends on a rolling temperature, even if a stainless steel strip such as SUS 301 or SUS 304 is cold-rolled at the same reduction ratio. When the steel strip is cold-rolled at a high temperature, generation of the deformation-induced martensite is suppressed, resulting in poor hardness of the cold-rolled steel strip. A lower rolling temperature accelerates transformation to deformation-induced martensite and raises hardness of the cold-rolled steel strip, on the contrary. Rising of hardness causes increase of deformation resistance, and so makes it difficult to flatten the shape of the steel strip.

SUMMARY OF THE INVENTION

The present invention aims at provision of a high-strength austenitic stainless steel strip excellent in flatness of shape with Vickers hardness of 400 or more. Improvement of flatness is attained by volumetric change during reversion from deformation-induced martensite to austenite so as to suppress shape deterioration caused by martensitic transformation, instead of flattening a shape of the steel strip in a martensitic phase as such.

The high-strength austenitic stainless steel strip proposed by the present invention has the composition consisting of C up to 0.20 mass %, Si up to 4.0 mass %, Mn up to 5.0 mass %, 4.0-12.0 mass % Ni, 12.0-20.0 mass % Cr, Mo up to 5.0 mass %, N up to 0.15 mass %, optionally at least one or more of Cu up to 3.0 mass %, Ti up to 0.5 mass %, Nb up to 0.50 mass %, Al up to 0.2mass %, B up to 0.015 mass %, REM (rare earth metals) up to 0.2 mass %, Y up to 0.2 mass %, Ca up to 0.1 mass % and Mg up to 0.10 mass %, and the balance being Fe except inevitable impurities with the provision that a value Md(N) defined by the formula (1) is in a range of 0-125. The steel strip has a dual-phase structure of austenite and martensite, which involves a reversed austenitic phase at a ratio more than 3 vol.%.

$$Md(N) = 580 - 520C - 2Si - 16Mn - 16Cr - 23Ni - 26Cu - 300N - 10Mo \quad \cdots\cdots(1)$$

The newly proposed austenitic stainless steel strip is manufactured as follows: A stainless steel strip having the properly controlled composition is solution-treated, cold-rolled to generate a deformation-induced martensite phase, and then re-heated at 500-700°C to induce reversion, whereby an austenitic phase is generated at a ratio of 3 vol.% or more in a matrix composed of the deformation-induced martensite. When the steel strip is reversed in a state charged with a load of 785Pa or more, it is further improved in flatness of shape.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The inventors have researched and examined, from various aspects, effects of conditions for manufacturing a meta-stable austenitic stainless steel strip, which generates deformation-induced martensite during cold-rolling, on hardness and flatness of the steel strip. As results of the researches, the inventors have found that heat-treatment to promote reversion from deformation-induced martensite to austenite causes volumetric change of the steel strip effective for improvement of flatness. High strength and excellent flatness are gained by properly controlling composition of steel as well as conditions for reversion. In the specification of the present invention, the wording "a steel strip" of course involves a steel sheet, and the same reversion to austenite is realized during heat-treatment of the steel sheet.

The composition of the austenitic stainless steel together with the conditions of reversion will become apparent from the following explanation.

C up to 0.20 mass %

C is an austenite former, which hardens a martensite phase and also lowers a reversion temperature. As the reversion temperature falls down, reversion to austenite is more easily controlled at a proper ratio suitable for improvement of flatness and hardness. However, precipitation of chromium carbides at grain boundaries is accelerated in a cooling step after solution-treatment or during aging as increase of C content. Precipitation of such the chromium carbides causes degradation of intergranular corrosion cracking resistance and fatigue strength. In

this sense, an upper limit of C content is determined at 0.20 mass %, so as to inhibit precipitation of chromium carbides by conditions of heat-treatment and a cooling speed.

Si up to 4.0 mass %

Si is a ferrite former, which dissolves in a martensite matrix, hardens the martensitic phase and improves strength of a cold-rolled steel strip. Si is also effective for age-hardening, since it promotes strain aging during aging-treatment. However, excessive addition of Si causes high-temperature cracking and also various troubles on a manufacturing process, so that an upper limit of Si content is determined at 4.0 mass %.

Mn up to 5.0 mass %

Mn is effective for suppressing generation of δ-ferrite in a high-temperature zone. An initiating temperature for reversion falls as increase of Mn content, so that a ratio of reversed austenite can be controlled with ease. However, excessive addition of Mn above 5.0 mass % unfavorably accelerates generation of deformation-induced martensite during cold-rolling, and makes it impossible to use the reversion for improvement of flatness.

Ni: 4.0-12.0 mass %

Ni inhibits generation of δ-ferrite in a high-temperature zone as the same as Mn, and lowers an initiating temperature for reversion as the same as C. Ni also effectively improves precipitation-hardenability of a steel strip. These effects are apparently noted at Ni content not less than 4.0 mass %. However, excessive addition of Ni above 12.0 mass % unfavorably accelerates generation of deformation-induced martensite during cold-rolling and so makes it difficult to induce the reversion necessary for flattening.

Cr: 12.0-20.0 mass %

Cr is an alloying element for improvement of corrosion resistance. Corrosion resistance is intentionally improved at Cr content of 12.0 mass % or more. However, excessive addition of Cr causes too much generation of δ-ferrite in a

high-temperature zone and requires increase of austenite formers such as C, N, Ni, Mn and Cu. Increase of the austenite formers stabilizes an austenitic phase at a room temperature and makes it hard to generate deformation-induced martensite during cold-rolling. As a result, a steel strip after being aged is poor of strength. In this sense, an upper limit of Cr content is determined at 20.0 mass %, in order to avoid increase of the austenite formers.

Mo up to 5.0 mass %

Mo effectively improves corrosion resistance of the steel strip and promotes dispersion of carbides as fine particles during reversion. In reversion treatment useful for flattening a shape of a steel strip, a re-heating temperature is determined at a level higher than a temperature for conventional aging treatment. Although elevation of the re-heating temperature accelerates release of strains, abrupt release of strains is suppressed by addition of Mo. Mo generates precipitates effective for improvement of strength during aging and inhibits decrease of strength at a reversion temperature higher than a conventional aging temperature. These effects are apparently noted at Mo content of 1.5 mass % or more. However, excessive addition of Mo above 5.0 mass % accelerates generation of δ-ferrite in a high-temperature zone.

N up to 0.15 mass %

N is an austenite former, which lowers an initiating temperature for reversion, as the same as C does. Reversed austenite can be controlled at a ratio suitable for flatness of shape and strengthening with ease by addition of N at a proper ratio. However, since excessive addition of N causes occurrence of blowholes during casting, an upper limit of N content is determined at 0.15 mass %.

Cu up to 3.0 mass %

Cu is an optional alloying element acting as an austenite former, which lowers an initiating temperature for reversion and promotes age-hardening during reversion. However, excessive addition of Cu above 3.0 mass % causes poor hot-workability and occurrence of cracking.

Ti up to 0.50 mass %

Ti is an optional alloying element, which promotes age-hardening and improves strength during reversion. However, excessive addition of Ti above 0.50 mass % causes occurrence of scratches on a surface of slab and troubles on a manufacturing process.

Nb up to 0.50 mass %

Nb is an optional alloying element, which improves strength during reversion but degrades hot-workability of a steel strip. In this sense, Nb content shall be limited to 0.50 mass % or less.

Al up to 0.2 mass %

Al is an optional alloying element, which serves as a deoxidizing agent in a steel-making step and remarkably reduces type-A inclusions harmful for press-workability. The effects of Al are saturated at 0.2 mass %, and excessive addition of Al causes other troubles such as occurrence of surface flaws.

B up to 0.015 mass %

B is an optional alloying element effective for inhibiting occurrence of edge cracks, which are derived from a difference of deformation resistance between δ-ferrite and austenite at a hot-rolling temperature, in a hot-rolled steel strip. However, excessive addition of B above 0.015 mass % causes generation of low-melting boride and rather deteriorates hot-workability.

REM (rare earth metals) up to 0.2 mass %

Y up to 0.2 mass %

Ca up to 0.1 mass %

Mg up to 0.1 mass %

Each of REM, Y, Ca and Mg is an optional alloying element, which improves hot-workability and oxidation resistance. Such the effects are saturated at 0.2 mass % REM, 0.2 mass % Y, 0.1 mass % Ca and 0.1 mass % Mg, respectively, and excessive addition of these elements worsens cleanliness of steel material.

The newly proposed steel strip further includes P, S and O other than the

above-mentioned elements. P is an element effective for solution-hardening but harmful for toughness, so that an upper limit of P content is preferably determined at a conventionally allowable level 0.04 mass %. S content shall be controlled to a lowest possible level, since S is a harmful element which causes occurrence of ear cracks during hot-rolling. The harmful influence of S can be inhibited by addition of B, so that allowable S content is preferably determined at 0.02 mass % or less. O generates nonmetallic oxide inclusions, which worsens cleanliness of steel and put harmful influences on press-workability and bendability, so that O content is preferably controlled at a ratio of 0.02 mass % or less.

A value Md(N) defined by the formula of Md(N)=580−520C−2Si−16Mn−16Cr−23Ni−26Cu−300N−10Mo: 0-125

According to the present invention, a shape of a stainless steel strip is flattened by volumetric change during re-heating to induce reversion from deformation-induced martensite, which is generated by cold-rolling, to austenite. For such the reversion, a value Md(N) representing stability of an austenitic phase against working is controlled in a range of 0-125 so as to generate deformation-induced martensite by cold-rolling after solution-treatment. The value Md(N) shall be not less than 0; otherwise cold-rolling at an extremely lower temperature, which is not adaptable for an industrial manufacturing process, would be necessary for generation of a martensite phase effective for improvement of strength. If the value Md(N) exceeds 125 on the contrary, an austenitic phase, which is generated during reversion, is re-transformed to martensite during cooling to a room temperature, resulting in degradation of shape.

A temperature for reversion: 500-700°C

When a solution-treated steel strip is cold-rolled, deformation-induced martensite is generated by the cold-rolling. The cold-rolled steel strip is then re-heated at a temperature to reverse the deformation-induced martensite to austenite. If the re-heating temperature is lower than 500°C, the reversion progresses too slow in an industrial point of view. However, a re-heating

temperature higher than 700°C extremely accelerates the reversion and also softens a martensite phase, so that it is difficult to stably bestow the steel strip with Vickers hardness of 400 or more. The too higher re-heating temperature also causes degradation of corrosion resistance due to sensitization derived from carbide precipitation.

A ratio of reversed austenite: 3 vol.% or more

Volumetric change during reversion from martensite to austenite is shrinkage of 10% or so, and a steel strip is flattened by the shrinkage deformation. Although a shape of a steel strip collapses due to volumetric expansion caused by transformation from austenite to martensite during cold-rolling, such collapse of the shape is eliminated by the shrinkage deformation during the reversion from deformation-induced martensite to austenite, which is realized by re-heating the cold-rolled steel strip. As a result of the experiments under various conditions, the inventors have found that a ratio of reversed austenite, which effects on flatness of a steel strip, is at 3 vol.% at least.

A load applied to a steel strip during reversion: 785Pa or more

A steel strip is held in a state good of shape by application of a tension to a strip coil or by gravity of a steel strip itself during reversion. Flatness of the steel strip is further improved by reversion under the condition that a load is applied to the steel strip with a pressboard or the like, since the reversion progresses while restrained. In this case, a load is preferably of 785Pa or more for each unit area, accounting high-temperature strength at the reversion.

EXAMPLE

Each stainless steel 250kg having the composition shown in Table 1 was melted in a vacuum furnace, cast to an ingot, forged, hot-rolled to thickness of 4.0mm, annealed 1 minute at 1050°C, and then pickled with an acid. After the steel strip was cold-rolled, it was re-heated 600 seconds to induce reversion. Conditions for cold-rolling and re-heating are shown in Table 2. In Table 1, stainless steels Nos.

1-8 have compositions which satisfy conditions defined by the present invention, while stainless steels Nos. 9-14 have compositions out of the present invention. In Table 2, stainless steels Nos. 1-10 are those processed under conditions according to the present invention, while stainless steels Nos. 11-19 are those processed under conditions out of the present invention.

Table 1: CHEMICAL COMPOSITIONS OF STAINLESS STEELS USED IN EXAMPLES

Steel No.	alloying elements (mass %)										others	Md(N)	Note
	C	Si	Mn	P	S	Ni	Cr	Mo	N	O			
1	0.125	1.43	2.80	0.025	0.015	5.89	18.02	0.98	0.089	0.0042		7.0	Inventive Examples
2	0.078	2.54	0.31	0.023	0.002	8.23	13.42	2.29	0.064	0.0058		83.3	
3	0.080	2.72	4.18	0.025	0.005	5.22	16.20	1.53	0.134	0.0068	B:0.008	31.3	
4	0.058	1.35	1.26	0.026	0.006	6.80	12.48	2.30	0.078	0.0074	Nb:0.28	124.5	
5	0.077	1.54	0.89	0.027	0.001	6.23	15.65	1.98	0.084	0.0084	Al:0.14	84.0	
6	0.080	3.75	0.30	0.033	0.008	8.42	13.65	2.28	0.076	0.0079	Ti:0.37,B:0.011	68.4	
7	0.082	2.73	0.37	0.028	0.018	5.91	12.59	1.52	0.115	0.0064	Cu:1.67,Nb:0.31	95.5	
8	0.018	0.37	2.21	0.032	0.009	6.23	17.58	0.24	0.080	0.0077	Ca:0.009,Y:0.05	83.6	
9	0.214	0.52	0.34	0.025	0.007	9.24	16.23	1.87	0.009	0.0056		-31.4	Comparative Examples
10	0.084	0.45	0.42	0.024	0.009	4.56	16.25	0.86	0.008	0.0059	Nb:0.23	152.8	
11	0.185	0.87	5.28	0.029	0.007	6.76	14.05	1.89	0.011	0.0060	Ti:0.34,Ca:0.005	-4.9	
12	0.102	1.78	3.45	0.035	0.018	2.03	19.00	1.52	0.065	0.0045	Ca:0.017	82.8	
13	0.128	0.24	1.98	0.019	0.022	7.00	12.89	4.23	0.123	0.0095	Cu:1.87	-13.8	
14	0.098	0.59	0.98	0.022	0.014	6.95	16.78	1.87	0.163	0.0088		16.3	

The underlines mean figures out of the present invention.

TABLE 2: EFFECTS OF COLD-ROLLING AND REVERSION

Ex. No.	Steel No.	a reduction ratio (%)	a temperature (°C) of reversion	hardness HV1	a ratio (vol.%) of reversed austenite	max. height (mm) of ears	Note
1	1	85	525	483	4	1.8	Inventive Examples
2	2	50	650	520	10	1.6	
3	2	60	625	488	8	1.4	
4	3	64	574	462	6	1.2	
5	4	35	650	523	13	1.5	
6	5	60	650	563	14	1.1	
7	5	70	647	487	14	1.2	
8	6	70	689	423	18	1.2	
9	7	50	543	503	6	1.8	
10	8	45	674	423	22	0.9	
11	1	85	732	375	25	1.1	Comparative Examples
12	2	50	480	391	2	5.9	
13	3	60	785	308	34	0.9	
14	9	90	650	386	2	6.7	
15	10	30	634	389	8	8.3	
16	11	85	589	305	4	0.8	
17	12	60	625	378	7	5.6	
18	13	85	653	356	2	6.5	
19	14	80	589	443	11	0.2	

The underlines mean figures out of the present invention.

It is noted from Table 2 that Inventive Examples Nos. 1-10 were stainless steel strips excellent in flatness with Vickers hardness of 400 or more in average. These steel strips had maximum height of ears controlled smaller than 2mm after the reversion.

Comparative Examples Nos. 11-13 are stainless steels having compositions in the range defined by the present invention. But, reversed austenite was not sufficiently generated in the steel of Example No. 12, since a re-heating temperature was below 500°C. The steels of Example Nos. 11 and 13 had Vickers hardness below 400, since a re-heating temperature therefor was higher than 700°C.

Comparative Examples Nos. 14-18 are stainless steel strips, which was poor of flatness at Vickers hardness of 400 or more due to compositions out of the range defined by the present invention. Especially, the steel of Example No. 15 was heavily deformed by re-transformation of reversed austenite to martensite during cooling due to a big Md(N) value above 125. The steel of Example No. 19 involved flaws, which originated in blowholes during steel making and casting steps, scattered on its surface due to excessive N content.

Each steel strip was sized to a sheet of 200mm in width and 300mm in length by cutting off both edges with width of 10mm, and pressed with a press board at a pressure shown in Table 3 in order to further improve flatness of the steel sheet. The steel sheet was re-heated 600 seconds to induce reversion under the pressed condition. Effects of a load applied to the steel sheet were investigated in relation with flatness of the re-heated steel sheet. Results are shown in Table 3, together with ratios of reversed austenite and averaged Vickers hardness (a load of 10kg).

It is noted from Table 3 that any steel of Example Nos. 1-6 had Vickers hardness of 400 or more in average and height of ears suppressed below 1.0mm due to application of the load during reversion. The relation of the applied load with the maximum height of ears proves that a shape of a steel sheet is effectively flattened

by application of a load of 785Pa or more.

TABLE 3: EFFECTS OF APPLIED LOADS DURING REVERSION ON FLATNESS OF STEEL SHEETS

Example No.	Steel No.	a reduction ratio (%)	a temperature (°C) for reversion	an applied pressure (Pa)	hardness HV1	a ratio (vol.%) of reversed austenite	Maximum height (mm) of ears
1	1	85	550	2944	577	4	0.8
2	2	50	604	3925	520	11	0.3
3	2	60	625	785	477	15	0.8
4	3	60	650	1569	462	6	0.4
5	3	60	700	8635	415	32	0.6
6	4	64	610	4416	534	8	0.2

According to the present invention as above-mentioned, an austenitic stainless steel strip excellent in flatness of shape with Vickers hardness of 400 or more is manufactured by properly controlling its composition and conditions for reversion so as to disperse reversed austenite in a matrix of deformation-induced martensite at a predetermined ratio. The proposed steel strip is also good of corrosion resistance. Due to such the excellent properties, the austenitic stainless steel is useful as various spring materials or high strength materials in a broad industrial field, e.g. press plates, stainless frames, plate springs, flapper valves, metal gaskets, wrapping carriers, carrier plates, stainless mirrors, damper springs, disk brakes, brake master keys, steel belts and metal masks.